

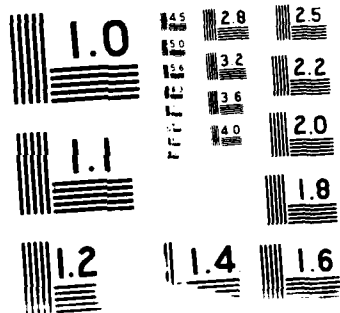
AD-A194 287 HYDROGEN STORAGE BY MOLECULAR POLYHYDRIDES(U) YALE UNIV 1/1
NEW HAVEN CONN DEPT OF CHEMISTRY R H CRABTREE
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Final Report

We set out to discover whether molecular polyhydrides $[MH_xL_y]$ (M = transition metal, $x = 3-9$, $L = 3^\circ$ phosphine) would be effective hydrogen storage agents. This three year period has taught us about some very unexpected new aspects of these complexes. The papers published under ARO sponsorship are very heavily cited and a new area of dihydrogen complexation has grown up within that time.

Nonclassical polyhydrides. Kubas et al. were the first to recognise that dihydrogen could bind to a metal without breaking the H-H bond in the complex $[W(H_2)CO_3(PCy_3)_2]$. We have shown that far from being a rare binding mode, dihydrogen binding occurs in this way in a wide variety of polyhydrides $[MH_xL_y]$. These had previously been assumed to have classical structures with all M-H bonds. We were able to show that in fact H-H bonds are present in about 50% of the cases examined. In these nonclassical complexes we can be sure that H-H bonds are present but we cannot yet say whether these are present in H_2 or H_3 fragments.

Hydrogen Transport Not only does H_2 bind, but it also dissociates rapidly and reversibly in certain of these nonclassical hydrides, notably $[IrH(H_2)bq(PPh_3)_2]$ (bq = benzoquinolate). We now find that this complex selectively transports H_2 through an organic solvent. Membrane transport is not only an important problem from the biological point of view but it has interesting commercial implications (unfortunately the Japanese seem to be following these up more vigorously than we are). Our's is the first system capable of transporting H_2 , however.

Hydrogen storage It is very likely that the rapid and reversible binding could be employed in hydrogen storage, but the cessation of funding by ARO has forced us to seek support from other sources, who are naturally more

interested in other aspects of the problem and so we are not pursuing this area at the moment.

The T_1 Method. Our most important contribution in this grant period has been the development of the T_1 method, which is already the standard method for distinguishing classical from nonclassical structures. It relies on the strong dipole-dipole coupling between the protons of the H-H bond. This effect is modulated by the rotation of the molecule to give a temperature dependent T_1 from which an approximate ($\pm 0.05 \text{ \AA}$) H-H distance can be obtained.

New Types of Nonclassical Polyhydride We have been interested in extending the range of L groups capable of giving polyhydrides, so that we could obtain greater thermal stability for practical applications of these materials. Up to now only 3° phosphines and, very rarely, cyclopentadienyl groups have served as L. We now find that a whole series of N-ligands can also act in this way. These should be much more robust and they are found to provide nonclassical structures, exactly the ones we need for H-storage applications. Examples of the new classes of polyhydride include TpReH_6 and BpReH_7 (Tp = tris(pyrazolyl)borate; Bp = bis(pyrazolyl)methane). These are the first N-stabilized polyhydrides. We have used the T_1 method to show that they are nonclassical, having the structures $\text{TpRe}(\text{H}_2)\text{H}_4$ and $\text{BpRe}(\text{H}_2)\text{H}_5$, respectively. The thermal stability of both complexes is high; they survive sublimation.

Quantitative results of the T_1 Method These are shown in the table on the following page.

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4d	<input type="checkbox"/>
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Stability Data	
Dist	Qual and/or Spec
A-1	<input checked="" type="checkbox"/>

Variable Temperature T_1 Data

Compound ^a	Temp(K) ^b	T_1 (min) ^c	$r(\text{\AA})$ ^d	$r(\text{\AA})$	structure ^e
CpRu(PPh ₃) ₂ H	238	300	1.87C		c
[IrH ₂ (CO) ₂ (PPh ₃) ₂] ⁺	210	245	1.81C		c
IrH ₅ (PCy ₃) ₂	<193	<820	<2.23C		c
ReH ₅ (H ₂)(PPh ₃) ₂	200 ^f	110 ^g	1.19C		nc
ReH ₅ (H ₂)(dpe) ^f	222	67	1.24C		nc
ReH ₅ (H ₂){P(<i>o</i> -C ₆ H ₄ F) ₃ } ₂	200	55	1.19C		nc
ReH ₅ (H ₂)(PCy ₃) ₂	<200	<60	<1.22C		nc
[ReH ₈ (PPh ₃)] ^{-h}	200	245	1.81C		c
Ru(H ₂)H ₂ (PPh ₃) ₃	266	30	1.16C		nc
[Os(H ₂)H ₃ (PPh ₃) ₃] ⁺	220	35	1.15C		nc
MoH ₄ (PMePh ₂) ₄	250	165	1.70C		c
WH ₆ (PMe ₂ Ph) ₃	235	181	1.73C		c
WH ₅ (PMePh ₂) ₄ ⁺	240	179	1.75C		c
W(H ₂)(CO) ₃ (Pi-Pr ₃) ₂	193	<5 ⁱ	<0.95C	0.84 ^j	nc
[FeH(H ₂)(dppe) ₂] ⁺	210	<8.5 ^{k,l}	<1.07C	0.89 ^m	nc
[IrH(H ₂)(bq)(PPh ₃) ₂] ⁺	200	8 ^l	1.01C	0.92 ⁿ	nc

^a solvents: CH₂Cl₂ or toluene at 250 MHz. unless stated. ^b at which the minimum T_1 is observed. From the theory of T_1 , this value is related to the H-H distance. ^c the T_1 at the minimum. ^d $\pm 0.02\text{\AA}$, calculated as described in the full paper (C = ca. 0.9). ^e classical, c; nonclassical, nc. ^f at 500 MHz. ^g from the theory, this value is equivalent to a T_1 (min) of

55ms. at 250 MHz. At the lowest temperature, the observed T_1 at 250 MHz. was indeed 55ms., and so we were very close to the minimum. ^h in d_6 -ethanol. ⁱ from the literature; original measurement at 200MHz, but T_1 value shown here calcd. for 250 MHz. ^j by neutron diffraction. ^k from the literature; original measurement at 200MHz, but T_1 value shown here calcd. for 250 MHz. ^l of the dihydrogen resonance. ^m by X-ray diffraction. ³ ⁿ by solid state NMR (literature measurement by K Zilm).

Bonding Model The bonding model we support involves $H_2(\sigma)$ to $M(d_\sigma)$ donation accompanied by a restricted amount of $M(d_\pi)$ to $H_2(\sigma^*)$ back donation. Excessive back donation naturally causes H-H cleavage since the $H_2(\sigma^*)$ being filled is antibonding in character. This explains the distribution of structures we observe. For example, in the series MH_4L_3 ($M = Fe, Ru, Os$; $L = 3^\circ$ phosphine), the Fe and Ru complexes are nonclassical and the Os complex is classical. It is well accepted that Os is a better π -donor than Fe or Ru. The same arguments also apply to the conversion of classical IrH_5L_2 to the nonclassical $[IrH_2(H_2)_2L_2]^+$ which we observe on protonation.

Biological Relevance. We have suggested that hydrogenase and nitrogenase bind H_2 in the nonclassical form. Not only does this account for the H/D exchange properties of the enzyme, but the relatively high oxidation states involved makes such binding reasonable on the basis of the bonding model.

Conclusion We have shown that H_2 complexes, far from being a rare class, are in fact widely distributed, and were even unrecognized in long known compounds. We feel that these new species have a very good chance of technological application, although whether this will happen in this country or elsewhere is not yet clear.

Publications acknowledging ARO support.

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Degrees awarded

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A. Habib, Ph. D., 1986

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